

CHEMICAL BOND CLEAVAGE DURING ASPHALTENE FORMATION¹

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An important question arising from experiments involving coal liquefaction processes is "which bonds are broken when solid coal is converted to liquids, or to soluble oils, asphaltenes, and preasphaltenes?" In earlier work² it was proposed that ether linkages were cleaved and hydrogenolysis occurred during treatment of coal with hydrogen-donor solvents at elevated temperatures. Thus, a limited number of model ether structures were shown to break in the presence of tetrahydroquinoline at 309°. It was also reported^{2,3} that solubilization could not be due to cleavage of single methylene bridges in coal. However, structures containing one methylene group in the bridge, such as diphenylmethane, are stable under the above conditions.

We presented data in a recent manuscript⁴ showing that other structure types undergo thermolysis under the conditions of asphaltene formation. A variety of diaryl- and triarylethanes and ethylenes were found to cleave at the central C-C bond; the derived products were characterized. Certain ethers were found to cleave accompanied by the formation of water.

We have now investigated a large variety of compounds containing structural linkages chosen, partly, from coal models suggested by Given,⁵ Weiser,⁶ and Hill and Lyon.⁷ Some bond types appear to cleave rapidly, others with difficulty, and some not at all. These compounds are arranged in groups and their relation to coal liquefaction is considered. Examples of bonds which break easily are those attaching large groups to the aromatic nucleus of phenols and phenol ethers. Parabenzylphenol is rapidly converted, principally, to toluene and phenol with a little benzene and p-cresol. Several products are produced from phenylethyl ether; benzene, toluene, ethylbenzene, phenol, ethane, ethylene, and water.

Implicit in a portion of the above discussion is another important question relating to the structural units in coal. For example, "does it contain any isolated, nonaromatic double bonds?" Hydrogen nmr does not show olefinic structure and carbon nmr is ambiguous. Our solution is based on the stitching and riveting reactions developed by H. C. Brown.⁸ Vitrinite, or a pyridine-soluble fraction of it, was reacted with diborane. Then the hydroborated coal was converted to a trialkylborane derivative by treating it with ethylene gas. Any trialkylborane formed within the coal structure was finally converted to a radioactive-labeled ketone by treatment with radioactive carbon monoxide, or with labeled cyanide ion, followed by hydrolysis. A determination of the specific carbon-14 activity enabled us to calculate the number of double bonds originally present. We are presently applying the above technique to other coal-derived materials. A summary of our data follows:

<u>Sample</u>	<u>Radio. Equiv., Wt.</u>	<u>No. of Carbons Per Double Bond</u>
Vitrinite (Ill. #6)	7300 g.	498
Pyridine-soluble Vitrinite	1500 g.	102
Blank	61000 g.	

References

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